




# Methods to Determine the Current Efficiency in AC Electrolysis

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## Abstract

The paper presents several methods (analytical, electromechanical and electronic) for determining the cathodic current efficiency of the metal deposition processes carried out by AC or pulse current. Based on the results of own experimental researches (for indium, cadmium, nickel, tin and zinc), the appropriate equations are given and the distribution of both faradaic and non-faradaic parts of charge (charging of the electrode double layer) is calculated.

**Keywords** Alternating current · Pulse electrolysis · Non-stationary electrolysis · Current efficiency · Current integrator

## 1 Introduction

The non-stationary electrolysis using alternating current has been the focus of interest for many years. In the first line, it concerns the obtaining of compact metal galvanic coatings [1, 2] or nanopore arrays used as templates for deposition of nanowires [3, 4], but in the second line—also other industrial processes like water electrolysis [5, 6] or metal refining (like copper [7, 8]).

In numerous papers [9, 10], the mechanisms of alternating current influence on the electrocrystallization process are considered. Investigations of process kinetics proved the possibility to obtain compact metal deposits from diluted solutions [11, 12], which is especially important during the wastewater treatment [13]. Algorithms to find the optimal forms of pulse current [14], description and diagrams of devices that allow realizing different modes are given [15, 16]. In many papers [17–20], the advantages of pulse electrolysis have been shown. However, some authors conclude

that pulse electrolysis has no advantages over stationary electrolysis [21].

It is interesting that the number of papers devoted to potentiostatic regime of pulse electrolysis is rather small. In the monographs of Bard & Allen [22] and Kostin and Kublanovski [9], various aspects of pulse electrolysis are considered, but without the question of current efficiency and the methodology of its determination. The paper of Potockaya et al. [23] concerns the influence of electrolysis regime on the concentrations of ions near to electrode, but without influence on current efficiency too.

On the other hand, the current efficiency is one of parameters characterizing electrochemical process and determining its practically economical usefulness in industry. If its determination in the case of DC electrolysis is relatively simple, then the use of AC current makes the matter more complicated. The impedance method used usually in laboratories is too expensive and rather useless for the work in industrial circumstances. At present, there is also no unified method to determine the total amount of electricity (charge) and the charge consumed by faradaic processes using alternating current at various regimes.

The aim of this work is to develop a simple method (based on digital coulometer or double-beam oscilloscope in connection with additional resistor) for determining of current efficiency at AC electrolysis various modes.

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## 2 Theoretical Consideration

The following processes can occur on the surface of cathode simultaneously, but naturally, with different rate:

1. ion reduction of some metals to the metallic state;
2. metal ion reduction to an intermediate oxidation state;
3. reduction of water molecules;
4. reduction of hydrogen ions;
5. reduction of molecules and particles which can be present in the solution as additives or impurities.

The flow of the above processes requires a certain charge, for the account of which the concept of the substance current efficiency has been introduced. Current efficiency of a metal or an alloy is most often determined gravimetrically, by the mass difference of a sample before and after the process, knowing the total consumed charge. However, in addition to the above processes, other processes that are not related to the electricity transmitted through the system can also occur on the surface of the electrode. For example, it is the dissolution of a metal from the surface of the cathode due to the reproporationation reaction [24], or as a result of the metal dissolution reaction due to the interaction with the hydrogen ion and also due to electrochemical corrosion from the non-equipotential electrode surface [25].

Thus, the measured coating mass (as a difference of the sample mass before and after the deposition process) is the mass difference of the electrochemically deposited and dissolved metal by various mechanisms. The use of this mass value for calculating the current efficiency of the metal is therefore not correct. Consequently, it is advisable to introduce the term of “an apparent cathodic current efficiency of metal.”

The application of various modes of alternating current electrolysis in electrochemistry has led to even greater difficulties in finding the value of metal current efficiency. A large number of different calculation methods [9], schemata and diagrams of different coulometers [26], as well as the term variants of “yield of metal” (“cathodic current efficiency of metal”, “effective current value efficiency of metal,” and “root-mean-square current efficiency of metal”) were proposed.

The current efficiency shows the part of current (or the charge), which is consumed in the electrode process under consideration [27]. The current efficiency always relates to a certain electrode reaction ( $CE_i$ ). Summing of all current efficiencies should result in 1 (100%) [22, 28].

It is obvious that the term of “cathodic current efficiency of metal” should be uniform and should not depend on the power regime of the electrochemical system. That

is, the use of constant, alternating or pulse current should not make changes or corrections to this formulation.

In spite of the fact that Faraday offered expressions connecting the charge and the mass (volume) of the product of the electrode reaction for stationary electrolysis, the use of his laws is possible for the alternating current mode of electrolysis too, but taking into account the part of current spent on non-faradaic processes.

When using alternating current, one part of electricity is spent on the processes not related to electrode reactions (electrical double layer (EDL) recharging), another part—on mutually opposite processes (deposition of metal during the cathodic half-cycle and its dissolution during the anodic one).

To change the electrode potential, in the absence of current consumed by various processes, the required charge is equal to [27]:

$$dq = C \cdot d\varphi,$$

where  $q$  is the charge,  $C$  is the capacity of the electrical double layer, and  $d\varphi$  is the change of electrode potential.

Given that

$$i = \frac{dq}{d\tau},$$

where  $i$  is the current density, and  $\tau$  is the time, we get:

$$i_{ch} = \frac{dq}{d\tau} = C \cdot \left| \frac{d\varphi}{d\tau} \right| \quad (1)$$

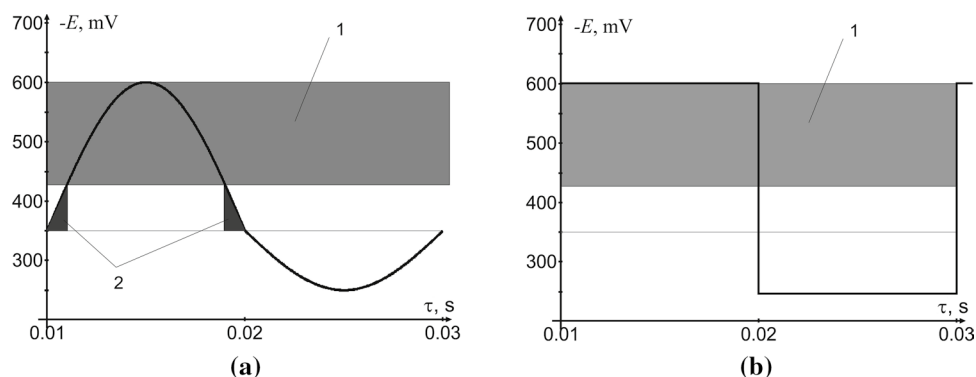
Hence, the more significant is the change of the potential over time  $\left( \frac{d\varphi}{d\tau} \right)$ , as well as the capacity of the electrical double layer, the greater is the charging current of EDL ( $i_{ch}$ ).

The analysis of Eq. (1) shows that the value of the charging current of EDL is influenced by electrode surface state, the near-electrode solution layer and the power regime of the electrochemical system. The change in the potential over time due to the steep leading edge will be greater than when using sinusoidal alternating current (Fig. 1a) or other forms of current for rectangular pulses (Fig. 1b). On the other hand, when using rectangular pulses, the efficiency of current used in the pulse will be higher [29], since with this pulse shape, the potential of the electrode almost instantaneously reaches a value at which the deposition of a metal or an alloy of the required composition begins. Similar conclusions have been reached by the Khorsani et al. [14].

Thus, with the use of alternating current of sinusoidal, quasi-sinusoidal, triangular, rectangular, saw tooth, and other forms, the fraction of current spent on the desired process directly depends on a number of factors, including frequency, voltage waveform, and amplitude value of the voltage in the pulse.



**Fig. 1** The ratio between the of “used” and “unused” charge during the electrodeposition of indium from an acid tartrate electrolyte using a quasi-sinusoidal asymmetric current (a) and potential pulses of a rectangular shape (b) (1—range of potential values in which discharge of indium (III) ions is possible, 2—ranges of direct pulse without deposition of indium; from [31])



Batishchev [30] presented methods for calculating the true cathodic and anodic current efficiencies, which take into account separately the charge consumed by depositing the metal in the cathodic half-cycle, and the charge consumed by dissolving the metal during the anodic half-cycle. However, these methods are based on the assumption that the true cathodic and anodic current efficiencies do not depend on the current density, what is contrary to the theoretical and practical fundamentals of electrochemistry [27].

When the current is switched on, processes are striving to achieve a stationary or quasi-stationary state. Thus, at some initial instant of time, the ratio between the charge consumed by the deposition of the metal, hydrogen evolution or by other parallel processes will be different in comparison with the time after achieving the quasi-stationary state.

Summarizing the foregoing, it is necessary to distinguish the following indicators for calculating the current efficiency:

1. total charge passed through the electrochemical system ( $Q_{\text{total}}$ );
2. charge spent on the faradaic processes ( $Q_F$ ).

Thus, using two different above values of the charge we obtain following expressions for calculating the current efficiency:

1. total current efficiency (or total charge) of the  $i$ -th substance at the main electrode ( $CE_{\text{total}}$ ):

$$CE_{\text{total}} = \frac{mzF}{MQ_{\text{total}}} = \frac{m}{kQ_{\text{total}}} \quad (2)$$

2. faradaic current efficiency (or the charge spent on the Faraday processes) of the  $i$ -th substance at the main electrode ( $CE_F$ ):

$$CE_F = \frac{mzF}{MQ_F} = \frac{m}{kQ_F} \quad (3)$$

where  $m$  is the mass of the substance underwent an electrochemical transformation at the electrode,  $z$  is the number of electrons participating in the elementary electrochemical act,  $F$  is the Faraday constant,  $M$  is the molar mass of the substance,  $\tau$  is the time of the process, and  $k$  is the electrochemical equivalent of the substance ( $k = \frac{M}{zF}$ ).

As follows from formulas 2 and 3, the difficulty of determining of the current efficiency value of the process being under consideration consists in finding of  $Q_{\text{total}}$  and  $Q_F$ .

### 3 Experimental

The experiments of metal deposition from the solution containing various ions were carried out, and in details described in our previous papers for: In [31], Cd [31], Ni [32], Sn [33], and Zn [34, 35]. Copper plates (grade of copper C 10200) of  $4 \times 10^{-4} \text{ m}^2$  were used as the main electrode. Graphite plates were used as auxiliary electrodes. The mass of the samples was determined to within 0.0001 g, using an analytical balance.

An asymmetric quasi-sinusoidal alternating current was produced by the signal amplification of a generator G3-33 by means of a device allowing separately regulate the amplitude of the direct and revertive pulses. A pulse current of a rectangular shape was produced with the help of a pulse generator G5-60. A dual-beam oscilloscope C1-99 was used to register the form of the signal and measure the amplitude value of the voltage. Potentiostatic pulses of a rectangular shape were produced with the help of a potentiostat IPC-Pro.

### 4 Results and Discussion

#### 4.1 Determination of the Total Charge

To determine the total charge passed through the electrochemical system ( $Q_{\text{total}}$ ), in condition of changing the



current during the process, it is necessary to perform the integration of the dependence of the current ( $I$ ) on time ( $\tau$ ) [9]:

$$Q_{\text{total}} = \int_0^{\tau} I d\tau \quad (4)$$

Several methods can be offered for the determination of  $Q_{\text{total}}$  which are combined in the following groups: analytical, electromechanical, and electronic.

A group of analytical methods helping to determine mathematically the charge can be used if the shape of current in the direct and reverse pulses is repeated throughout the process, and can be described by a some function.

Figure 2 presents the current–time dependence of cadmium electrodeposition from acidic electrolyte [31] using alternating asymmetric quasi-sinusoidal current.

The total charge for this mode can be calculated using the following formula [32]:

$$Q_{\text{total}} = n \cdot \left( \int_0^{\pi} |I_{\text{max}}^k \cdot \sin(2 \cdot \pi \cdot f \cdot \tau)| d\tau + \int_{\pi}^{2\pi} |I_{\text{max}}^a \cdot \sin(2 \cdot \pi \cdot f \cdot \tau)| d\tau \right) \quad (5)$$

where  $n$  is the number of periods of current oscillations during the electrolysis time,  $I_{\text{max}}^k$  is the amplitude value of the current in the cathodic half-cycle, A;  $I_{\text{max}}^a$  is the amplitude value of the current in the anodic half-cycle, A;  $f$  is the frequency of alternating current, Hz; and  $\tau$  is the time, s.

The values of the total charge passed through the galvanic bath for 10 min ( $n=30,000$ ) for the modes shown in Fig. 2a, b are given in Table 1.

When using a pulse current of a rectangular shape (galvanostatic pulses), several particular modes are possible:

- unipolar pulse current (direct pulse—pause);
- reverse mode (direct pulse—reverse pulse);
- other modes (direct pulse of large amplitude—direct pulse of small amplitude, program modes).

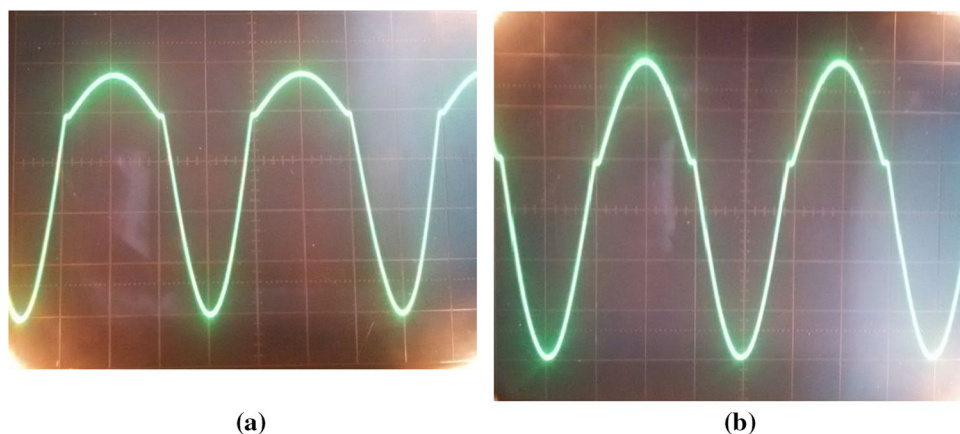
We confine ourselves to the consideration of the first two modes within the framework of this article.

For a unipolar pulse current

(“the provided current” is constant during the pulse), it is recommended to use formula [32]:

$$Q_{\text{total}} = \frac{I_{\text{max}} \cdot \tau_{\text{pulse}}}{\tau_{\text{pulse}} + \tau_{\text{pause}}} \cdot \tau = n \cdot I_{\text{max}} \cdot \tau_{\text{pulse}} \quad (6)$$

**Fig. 2** Oscillogram of asymmetric alternating current (frequency 50 Hz) for electro-deposition of cadmium [31] at different current densities  $i$ . **a**  $i_{\text{max}}^k = 1.0 \text{ A/dm}^2$ ;  $i_{\text{max}}^a = 0.25 \text{ A/dm}^2$ ; **b**  $i_{\text{max}}^k = 1.0 \text{ A/dm}^2$ ;  $i_{\text{max}}^a = 0.5 \text{ A/dm}^2$



**Table 1** Values of  $Q_{\text{total}}$  passed through a galvanic bath of cadmium plating in 10 min, for the modes shown in Fig. 2. (from [31, 32])

mode	$i_{\text{max}}^k, \text{ A/dm}^2$	$I_{\text{max}}^k, \text{ A}$	$i_{\text{max}}^a, \text{ A/dm}^2$	$I_{\text{max}}^a, \text{ A}$	$Q_{\text{for one period}}$		$Q_{\text{total}} = n \cdot (Q_k + Q_a), \text{ C}$
					$Q_k, \text{ C}$	$Q_a, \text{ C}$	
1	1.00	0.04	0.50	0.02	$2.55 \cdot 10^{-4}$	$1.27 \cdot 10^{-4}$	11.46
2	1.00	0.04	0.25	0.01	$2.55 \cdot 10^{-4}$	$0.64 \cdot 10^{-4}$	9.57



to insert a resistor (50  $\Omega$ ) with the galvanic bath having a resistance higher than resistance of the electrochemical system. The use of double-beam oscilloscope allows to observe simultaneously the voltage drop on the cell with and without additional resistor.

In the oscillograms shown in Fig. 3, we can see that the voltage drop at the additional resistor (upper beam) does not change with the pulse time, whereas the voltage drop on the resistance of the galvanic bath during the pulse (the lower beam) changes. The changes of used frequency in the range 100–1667 Hz do not change the shape of signal observed on resistor, while at the same time, such changes have been seen for the cell without resistor, especially if the frequency has grown. Thus, measuring the voltage drop at the additional resistor allows to find the amplitude value of the current in the pulse using Ohm's law.

When using the reverse mode of pulse electrolysis for determination of  $Q_{\text{total}}$ , the following formula should be used:

$$Q_{\text{total}} = \frac{|I_{\text{max}}^{\text{dir}}| \cdot \tau_{\text{dir}} + |I_{\text{max}}^{\text{rev}}| \cdot \tau_{\text{rev}}}{\tau_{\text{dir}} + \tau_{\text{rev}}} \quad (7)$$

$$= n \cdot \left( |I_{\text{max}}^{\text{dir}}| \cdot \tau_{\text{dir}} + |I_{\text{max}}^{\text{rev}}| \cdot \tau_{\text{rev}} \right)$$

where  $|I_{\text{max}}^{\text{dir}}|$  is the absolute amplitude value of the current in the direct pulse, A;  $|I_{\text{max}}^{\text{rev}}|$  is the absolute amplitude value of the current in the reverse pulse, A;  $\tau_{\text{dir}}$  is the direct pulse duration, s;  $\tau_{\text{rev}}$  is the reverse pulse duration, s; and  $\tau$  is the process duration, s.

In the proposed expression, it is necessary to take absolute (without regard to polarity) values of the current in the direct and reverse pulses.

The here-mentioned methods are applicable to other forms of current: triangular, sinusoidal with cutoff, and sinusoidal current with a constant component. However, the considered group of methods for determining the total charge

passed through electrochemical system is only suitable if the current in the pulse does not change in time, or its change proceeds according to some law, and can be described by a mathematical expression (for example, if the shape of the sinusoidal current is not distorted by electrochemical system).

It should be noted that in some non-stationary modes the amplitude value of the current or the electrode potential at the initial moment of time differs from such values after achievement of the quasi-stationary state [34, 35] (Fig. 4).

This circumstance does not allow using a group of analytical methods to determine the total charge in relation to the potentiostatic mode of pulse electrolysis and creates the prerequisites for the development of other groups of methods.

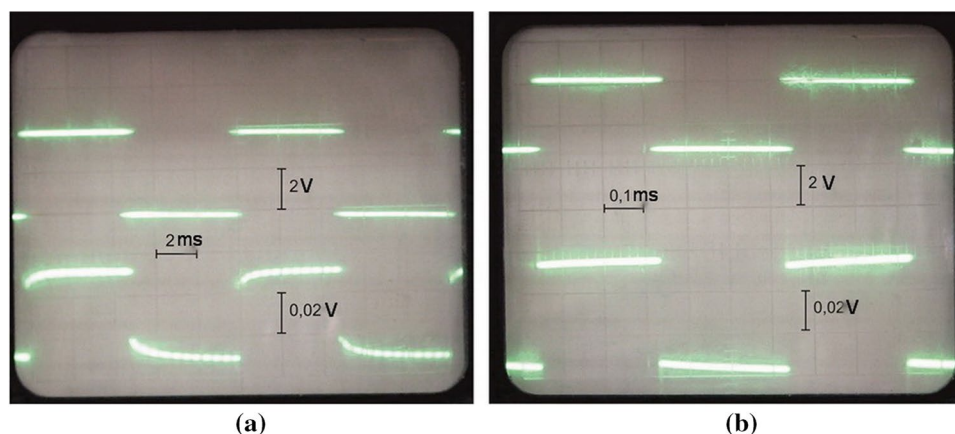
Electromechanical methods for determining the total charge in pulse electrolysis are of little use, because they do not allow recording the instantaneous values of the current of the pulse with duration less than a second with sufficient accuracy [36].

In this connection, the most interesting is the group of electronic methods in which instantaneous values of the current are recorded through short intervals of time with the help of special instruments.

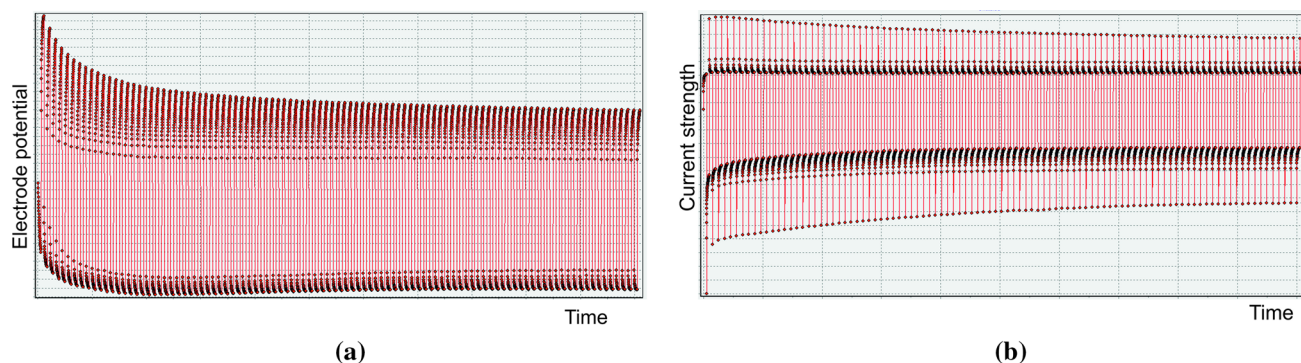
At present, a sufficiently large number of electronic current integrators are proposed which give the opportunity to determine the total charge passed through the circuit. However, most of those integrators are designed to work only with direct current [37]. To use the alternating current and reverse modes, it is necessary to apply special integrators having high operating speed and allowing to record instantaneous values of the current.

For these purposes, it is possible to use a digital coulometer, which has the following principle: a reference (calibrated) resistor  $R_0$  (having resistance for example, of 1  $\Omega$ , calculated for the current flowing through) is inserted in the circuit in series with the electrochemical cell (Fig. 5). If the current in the system is higher than the

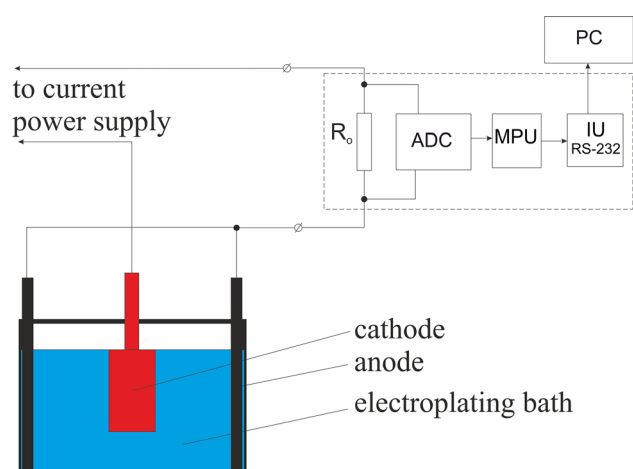
**Fig. 3** Oscillograms of different modes of pulse electrolysis (upper beam is the voltage drop at the additional resistor (50  $\Omega$ ; lower beam is the voltage drop at the galvanic bath of nickel plating) [32]







**Fig. 4** Change of the potential in time under galvanostatic mode (a) and of current under potentiostatic mode (b) of pulse electrolysis in acidic lactate electrolyte of zinc plating [35]



**Fig. 5** Scheme of the proposed digital coulometer ( $R_0$  is the reference resistor, ADC is the analog–digital converter, MPU is the microprocessor unit, IU RS-232 is the RS-232 interface unit, and PC is the personal computer)

one for which the resistor is designed, it is necessary to use a set of shunts, and take this into account in the results.

The value of current may be calculated by measuring the potential drop on a reference resistor. Voltage measurements are carried out through certain time intervals, which are determined by the frequency of the used current (the higher is the frequency, the shorter time interval is).

It has been experimentally established that the highest accuracy is observed when using a digital storage oscilloscope (for example, Tektronix TDS 1002B, TDS 3012B) connected in parallel to a reference resistor having a precise value of electrical resistance (for example, 1  $\Omega$ ). This method is the most suitable for laboratory studies aimed at establishing the optimal modes of pulsed electrolysis.

The proposed designs of current integrators will allow operating with currents of different shapes; therefore, they are universal.

## 4.2 Determination of Charge Spent on Faradaic Processes

Obtaining information on the dependence of the current of the process in time makes it possible to calculate the charge consumed by the entire process as a whole, and to calculate  $CE_{\text{total}}$ . It is possible to estimate the charge consumed only for Faraday processes, and, therefore, to calculate  $CE_F$ , using electrochemical coulometers [37].

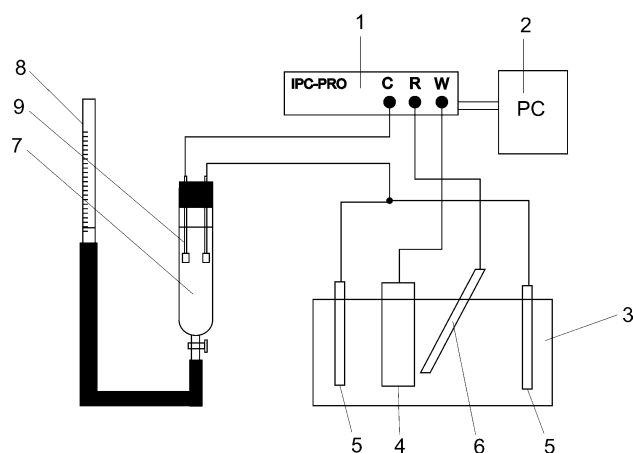
In the literature, there are quite contradictory data about the ratio of the current consumed by faradaic and non-faradaic processes. So, in [38] there is information that the time of EDL recharging is a fraction of a millisecond and, therefore, the contribution of the non-faradaic processes should be taken into account only at high frequencies (above 1000 Hz). However, there are experimental results in [39], from which it follows that an increase in the current frequency from 10 to 100 Hz (at a constant amplitude value of the polarizing current) causes that the part of current consumed by faradaic processes is reduced by 25%.

To choose the type of a coulometer, it is necessary to proceed from the fact that opposite processes (for example, deposition and dissolution of a metal) should not pass through the surface of the electrodes during the cathodic and anodic half-cycles. In this connection, the gas oxygen–hydrogen coulometer is the most suitable, consisting of two platinum electrodes immersed in a solution of alkali or sulfuric acid in a special vessel for accurate determination of the volume of the gas mixture (Fig. 6).

Thus, by measuring the total volume of the gas, it is possible to calculate approximately the charge passed through the system during the cathodic and anodic pulses and consumed only by faradaic processes (Table 2). Subtracting this value from the total of spent charge, we can find the charge consumed by non-faradaic processes (for example, the recharging of electrical double layer).

Examining the operation of this coulometer at different modes, we have found that the accuracy of charge





**Fig. 6** Device for measuring the charge spent on Faraday processes (1—potentiostat, 2—computer, 3—electrochemical cell with the test solution, 4—working electrode, 5—auxiliary electrodes, 6—reference electrode, 7—gas coulometer, 8—buret, 9—coulometer electrodes)

determining is high enough, and the error does not exceed 0.1%. However, to achieve high accuracy, it is recommended: to ensure a high degree of tightness of the system; to use burets having the corresponding size as a device for determining the volumes of released gases; to saturate the solution by gaseous oxygen and hydrogen, by “dummy” operation of this device before starting the research; to eliminate the possibility of cathodic oxygen reduction.

To fulfill the last point of the recommendations, it is necessary to ensure such conditions under which the discharge of hydrogen ions on the cathode would pass with the rate much higher than the rate of oxygen reduction. To achieve this, it is proposed to use acid solutions instead of solutions of alkalis, as in an acidic environment the discharge

of hydrogen ions is greatly facilitated, with an almost unchanged oxygen reduction rate.

On Table 2, we can see the values both of total and faradaic charges passed during the electrodeposition of zinc from the acid electrolyte with the addition of lactic acid [34].

The values of  $E_1$  and  $E_2$  parameters were chosen experimentally so that to have unipolar regime (during the half of period the current is null) and reverse regime when during the half of period there is cathodic (or anodic) current (see Fig. 7a, b).

It should be noted that with values of  $E_2$  potential less negative than  $-1000$  mV, a change in the current flow direction is observed in this solution (for some time at  $E_2$  values, the electrode is polarized anodically) (Fig. 7). This leads to the fact that the part of current consumed by EDL recharging decreases.

As we can see from the data presented in Table 2, the fraction of non-faradaic current is greater in reverse modes in comparison with unipolar modes.

The disadvantage of using an electrochemical coulometer to study the processes using alternating current is the fact that both the coulometer and the galvanic bath are complex systems described as a set of active and reactive resistances. Therefore, the coulometer connected in series will influence on the processes in galvanic bath [38].

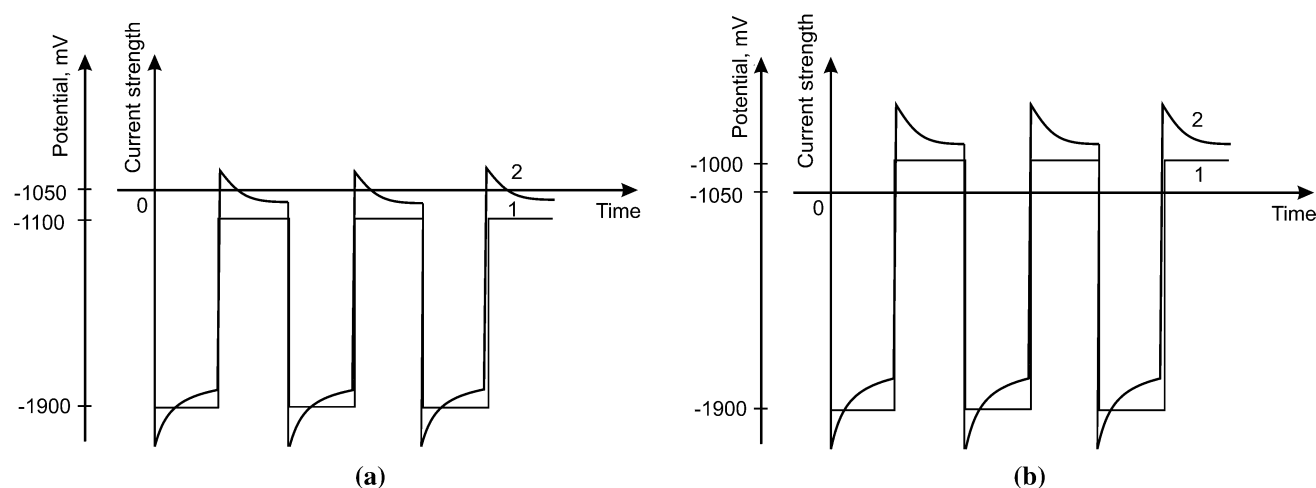
For this reason, the data given in Table 2 can only be used for a comparative assessment of influence of the electrolysis mode on the ratio between part of faradaic current and the current of EDL recharging. The absolute values given in Table 2 include the recharging current of EDL of all the electrodes of the system under study, as well as the coulometer electrodes.

Taking into account that the recharging current of EDL is directly proportional to EDL capacity, it is possible to

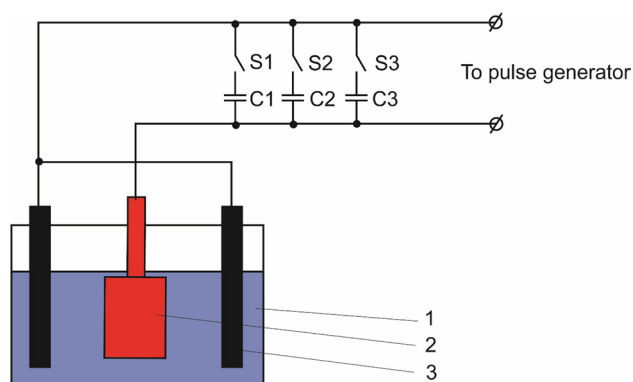
**Table 2** The ratio between the total charge ( $Q_{\text{total}}$ ) and the charge spent on faradaic processes ( $Q_F$ ) under various modes of electrodeposition of zinc from acid electrolyte with the addition of lactic acid (from [32, 34, 35])

No.	Electrolysis mode	Electrolysis mode	$Q_{\text{total}}$	$Q_F$	$\frac{Q_F}{Q_{\text{total}}} \cdot 100\%$
1.	$E_1 = -1900$ mV $E_2 = -1200$ mV $\tau_1 = \tau_2 = 0.25$ s	Unipolar	$45.73 \pm 0.24$	$42.19 \pm 0.66$	$92.26 \pm 2.26$
2.	$E_1 = -1900$ mV $E_2 = -1100$ mV $\tau_1 = \tau_2 = 0.25$ s	Unipolar	$45.33 \pm 0.50$	$41.84 \pm 0.67$	$92.30 \pm 2.93$
3.	$E_1 = -1900$ mV $E_2 = -1000$ mV $\tau_1 = \tau_2 = 0.25$ s	Reverse	$51.60 \pm 0.98$	$38.83 \pm 1.12$	$75.25 \pm 6.36$
4.	$E_1 = -1900$ mV $E_2 = -1200$ mV $\tau_1 = 0.25$ s $\tau_2 = 0.1$ s	Unipolar	$48.42 \pm 0.11$	$41.91 \pm 0.69$	$86.56 \pm 2.16$
5.	$E_1 = -1900$ mV $E_2 = -1200$ mV $\tau_1 = 0.1$ s $\tau_2 = 0.25$ s	Unipolar	$44.63 \pm 0.03$	$40.29 \pm 0.66$	$90.28 \pm 1.89$
6.	$E_1 = -1900$ mV $E_2 = -1200$ mV $\tau_1 = 0.1$ s $\tau_2 = 0.5$ s	Unipolar	$46.97 \pm 0.17$	$41.36 \pm 0.67$	$88.06 \pm 2.25$
7.	$E_1 = -400$ mV, $E_2 = -000$ mV, $\tau_1 = \tau_2 = 0.25$ s	Reverse	$54.92 \pm 1.21$	$38.33 \pm 1.07$	$69.79 \pm 7.16$





**Fig. 7** Dependence of the electrode potential (1) and current (2) in time under the potentiostatic mode of pulse electrolysis in acidic lactate electrolyte of zinc plating: **a** unipolar mode; **b** reverse mode; [35]



**Fig. 8** Device to determine the dependence of the charge spent on Faraday processes on the pulse current frequency (1—bath with electrolyte; 2—working electrode; 3—auxiliary electrodes; C1, C2, C3—capacitors; S1, S2, S3—toggle switches)

propose the system model (Fig. 8), in which capacitors are connected in parallel with the galvanic bath. At the same time, the total capacity of the system will increase; hence, the part of current consumed by non-faradaic processes will also increase. Thus, it will be possible to estimate the dependence of the charge consumed by faradaic processes on the frequency of pulse current.

The appropriate experiment was carried out in an acidic lactate electrolyte of tinning [33]. Galvanostatic regime with the current pulses of a rectangular shape (current density amplitude of  $3 \text{ A/dm}^2$ ) was applied in the experiments. The value of capacity of the additional capacitors has been changed from 0 to  $42 \mu\text{F}$ , which is comparable to EDL capacity of the flat electrode ( $20 \mu\text{F/cm}^2$ ) [40]. As the investigations showed, the influence of the pulse current frequency (up to 250 Hz) with different values of the

**Table 3** Dependence of the current efficiency of tin deposition on the pulse current frequency with different capacity values of the additional capacitor (from [33])

Capacity of the additional capacitor, $\mu\text{F}$	Pulse current frequency (duty cycle 2), Hz	Current efficiency of tin, %
0	50	95.49
	100	94.52
	250	92.53
10	50	92.48
	100	91.34
	250	87.67
20	50	92.51
	100	94.88
	250	89.77
42	50	91.91
	100	88.89
	250	87.74

additional capacity on the current efficiency of tin is insignificant (Table 3), and that allows to neglect the part of current consumed by non-faradaic processes. The obtained by us results are consistent with the results given in [9].

## 5 Conclusions

1. For the determination of total charge passed through the system,  $Q_{\text{total}}$ , the most acceptable are analytical methods and the using of electronic integrators of current (coulometers).
2. The comparison of results on current efficiency of AC electrochemical processes obtained by various authors





needs the knowledge about methods used for determining of the charge and methodology of calculating. Otherwise, there is no possibility to compare those results.

3. Schemes of devices and methods for determining Faraday and non-faradaic current components with pulse electrolysis described in this paper allowed to establish that

- at sufficiently low frequencies (less than 250 Hz), the part of current consumed by EDL recharging is negligible;
- when using the reverse mode of electrolysis, the part of non-faradaic component increases.

4. To find the value of the total charge with reverse current (“direct pulse–reverse pulse” mode), it is necessary to use absolute (without regard to polarity) values of the current in the direct and reverse pulses.
5. The use of analytical methods is possible only under the condition that the current during the pulse is constant or changing according to determined known function.
6. The energy efficiency of processes occurring with change of current and potential in time is less than when using direct current, since part of electricity in using alternating current is spent on non-faradaic processes. The experimental research makes possible to find the most optimal modes in which the part of current consumed by the faradaic processes is maximal.

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